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Comment on "Structural Prediction and Phase Transformation Mechanisms in Calcium at High Pressure"

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To resolve the discrepancy between experiment [1] and theory [2] regarding the stability of the simple cubic (sc) phase of Ca under pressure, Yao *et al.* [3] have performed metadynamics simulations and enthalpy analysis. They concluded that the sc structure becomes thermodynamically stable around 40 GPa and 50 K due to anharmonic free energy contributions. Here we show that this conclusion is an artifact of the 2-electron projector augmented wave (PAW) pseudopotential (PP) used in [3]. When semi-core states are included as valence electrons, the result is reversed and the sc structure is not preferred even at room temperature.

First, we would like to point out that it is not sufficient to use a 2-electron PP of Ca to explore its anharmonic free energy surface. In Fig. 1(a) we show the phonon dispersion curves of sc Ca at 45 GPa obtained with a 10-electron norm-conserving PP (see Ref. [2] for computational details). The frequencies at high-symmetry points are also computed with 10- and 2-electron PAW PP's by diagonalizing the dynamical matrix of an 8-atom supercell. The 2-electron PP results disagree with the rest and do not even yield imaginary frequencies at the X and M high-symmetry points.

We have investigated the stability of the sc phase at finite-temperature by comparing its Gibbs free energy with that of the previously reported *Pnma* structure [2] and a new $I4_1/amd$ structure, which we obtained by a random search method [4]. Yao *et al.* [3] have also found this structure using a genetic algorithm search. To compute free energies, we performed molecular dynamics (MD) simulations with the VASP code [5, 6] in a canonical ensemble on supercells consisting 32 and 64 atoms. Bigger supercells with 108 atoms for $I4_1/amd$ and 125 atoms for sc are also considered to verify the results. The calculations were performed with 2- and 10-electron PAW PP's, 11 Ha plane-wave cutoff, and the PW91 generalized gradient approximation parameterization for the exchange-correlation functional. The Brillouin zone was sampled at the Γ-point for the 108- and 125-atom supercells, and $2 \times 2 \times 4$ and $2 \times 2 \times 2$ Monkhorst-Pack grids were used for the 32- and 64-atom supercells, respectively. The equations of motion were integrated with ionic time steps of 1 fs and the ionic temperature was controlled with a Nosé-Hoover thermostat. Initially, the structures were allowed to equilibrate for 2 ps at 300 K. The simulations were then carried out for 3 ps to gather statistical information.

Using the same simulation parameters as in [3], the sc structure appears to have the lowest enthalpy at 300K as shown in Fig. 1(b). However, when we change the PP to include semi-core states, $I4_1/amd$ becomes more stable. Since entropic effects are essential for describing temperature-drived transition, we have also computed the Gibbs free energies of the candidate structures. The phonon entropy contribution is obtained from the vibrational density of states, which is the Fourier transform of the velocity autocorrelation function. As shown in Fig. 1(c), a 2-electon PP leads to sc having the lowest Gibbs free energy, while $I4_1/amd$ is preferred with the 10-electron PP. We obtained the same result with the larger supercell simulations as well. Comparing Fig's 1(b) and (c), it is interesting to note that anharmonic effects appear to play a significant role for the relative stability only with the 10-electron PP.

Our conclusion is that the stability of sc Ca has not been demonstrated theoretically yet and the discrepancy between theory and experiment remains unresolved. Further studies which may require the use of more accurate methods and measurements are necessary. A possible explanation could include fluctuations and distortions among several quasi-degenerate structures, as proposed by Yin *et al.* [7].

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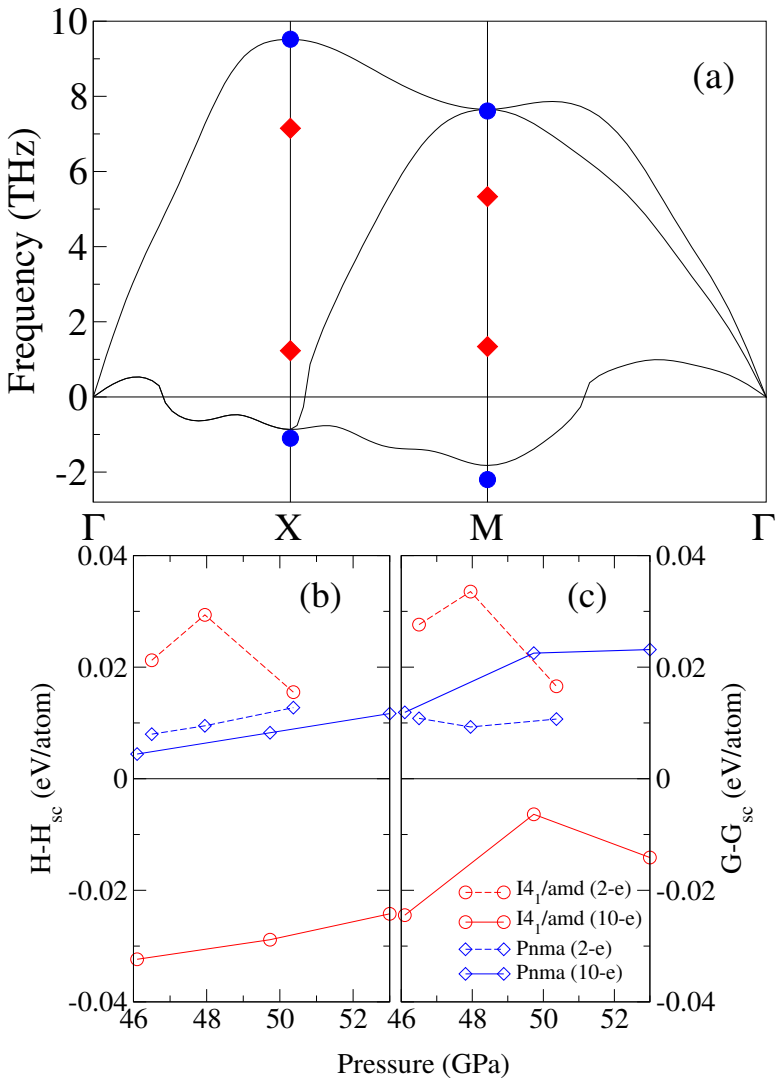

FIG. 1: (a) Phonon dispersion curves from linear response theory (10-electron OPIUM PP) and frequencies at X and M calculated with a 2-electron PAW PP (diamonds) and a 10-electron PAW PP (circles). Imaginary frequencies are shown as negative values. (b) Enthalpies and (c) Gibbs free energies relative to sc from 32-atom cell MD at 300K. Dashed and solid lines indicate relative energies with respect to sc obtained with 2- and 10-electron PP's, respectively.

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